Improving the properties of polymer blends by reactive compounding

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CHAPTER 9 IMPROVED TOUGHNESS VERSUS PROCESSING PARAMETERS.

Abstract.

The mechanical properties of the blend made with our new method have been investigated as a function of the processing parameters. By changing the parameters of the process we both change the conversion of the monomer in the dispersed phase and the mechanical properties of the blend. In this chapter we have to determine which parameters are critical for improving the mechanical properties of the blend formed by reactive compounding.
All the (PS/HDPE and PS/PP) blends formed with our new method of reactive compounding have an elongation at break which is much larger than the elongation at break of pure PS for almost all sets of processing parameters. Imperative to this was that a pressure built up section was present in front of the kneading section. The mechanical properties did not improve if the dispersed phase consisted of PMMA or PET (possibly because of the absence of a graft-reaction). No increase of elongation at break and impact value is found if HDPE is mixed with PS without adding other materials (such as reactive materials).

1 Introduction.

In the previous chapters some of the most important parameters for reactive compounding have been studied. For the reactive compounding process the temperature profile and the position of a pressure build-up section, a kneading section, and a transporting section in the extruder influence the formation of an alloying agent. Part of the monomer and initiator reacts in the dispersed phase and part diffuses out of the dispersed phase and reacts in the matrix phase. This has been measured and modelled and the molecular number distribution of the alloying agent formed has been calculated in chapter 5. The parameters needed such as the temperature of the melt in the extruder as a function of the processing parameters have been described in chapter 6. The morphology obtained in the intermeshing corotating-twin screw extruder has been studied in chapter 7. Computer modelling of the conversion of monomer in the dispersed phase during reactive compounding in an intermeshing corotating twin screw extruder has been described in chapter 8.
In chapter 7 it was mentioned that the size of the dispersed phase has an optimal value for toughness of the blend if the matrix is PS. From the literature it is known that some amorphous polymers tend to deform by crazing and some are ductile. Kramer et al (1) ascribed this transition to the fact that an increasing network density results in a higher surface

tension which hampers the void formation process of crazing. The other factor which determines the toughness of polymer-rubber blends is the adhesion between the dispersed phase of a blend and the matrix. Wu (2) found that the distance between the particles of the dispersed phase of a blend should be smaller than a certain critical inter-particle distance. The minimum adhesion required for toughening was also discussed. It was found that the critical size of the dispersed phase of a blend depends on its elastomer contents. The highest toughness was found to occur at an optimum particle size of 2- 5 μm.

1.1 Theory, Mechanical properties and morphology.

When looking at the mechanical properties of polymers it is useful to classify the existing polymers such as thermoplastics with respect to their physical composition. In all cases except the single phase material the morphology comes into play. The continuous phase is determining the general behaviour, but the dispersed phase will contribute in various ways. This depends on the volume fraction and the distance between the dispersed entities. Only amorphous polymers can be single phase while semi-crystalline polymers are always two-or more phase systems. In the rubbery state the material has little structural strength unless the material is cross linked chemically. A material is a thermo-plastic elastomer (TPE) if the cross-links are not of chemical but of physical nature (crystallites and/or a second solid phase in a copolymer). The stability of the physical network in a TPE is often achieved by the phase separation of the different segments.
Comparable considerations are valid for the mechanical properties of mixtures of polymers (blends). Yet there still is a lot of dispute about the mechanical properties, such as elongation at break and notched Izod impact strength and the relation with the morphology of blends. Two important aspects that have been stated in the literature are the need for a small size of the dispersed phase and adhesion between both phases. The influence of the size of the dispersed phase on the mechanical properties of polystyrene blends have been studied by van der Sanden (3). It was claimed that in this case only the Inter particle Distance (ID) between the dispersed phase particles in a blend determines whether a blend of PS with another polymer will have a brittle fracture or ductile fracture. If the value of ID is larger than the 'critical inter particle distance' (ID_c) brittle fracture of the ligament will occur. If brittle fracture cannot occur complete deformation of the ligament will take place, eventually leading to a fully ductile macroscopic fracture behaviour. The calculations of van der Sanden indicate that the material chosen for the dispersed phase will have no influence on the effectiveness of reactive blending. In this thesis it will be investigated whether the blends described in this thesis have improved mechanical properties because both phases have adhesion with each other by chemical linking of the dispersed phase to the matrix, figure 1a, b chapter 10. This will be investigated in the next chapter. Such a structure is also found in TPE's such as

styrene-ethylene-butadiene-styrene (SEBS) where the EB part of the chain is chemically linked to the S part. The physical properties and the theories needed for calculations of the properties of the polymers used in this thesis can be found in the handbook edited by Mark (4).

1.2 The conversion in the dispersed phase of a PS/HDPE blend.

The conversion of the reaction in the dispersed phase is shown in figure 1a. The reaction velocity is modelled with an Arrhenius equation (the constants are shown in the figure):

$$k_{ov} = Ae^{\frac{E_a}{RT}} \qquad [m^3 / mol\ s] \qquad (1)$$

Several effects influence the reaction velocity such as the temperature in the melt which increases with increasing rotational speed. However mass transport out of the dispersed phase also increases with increased mixing. Therefore the conversion has a maximum as a function of the rotational speed of the extruder in figure 1a.

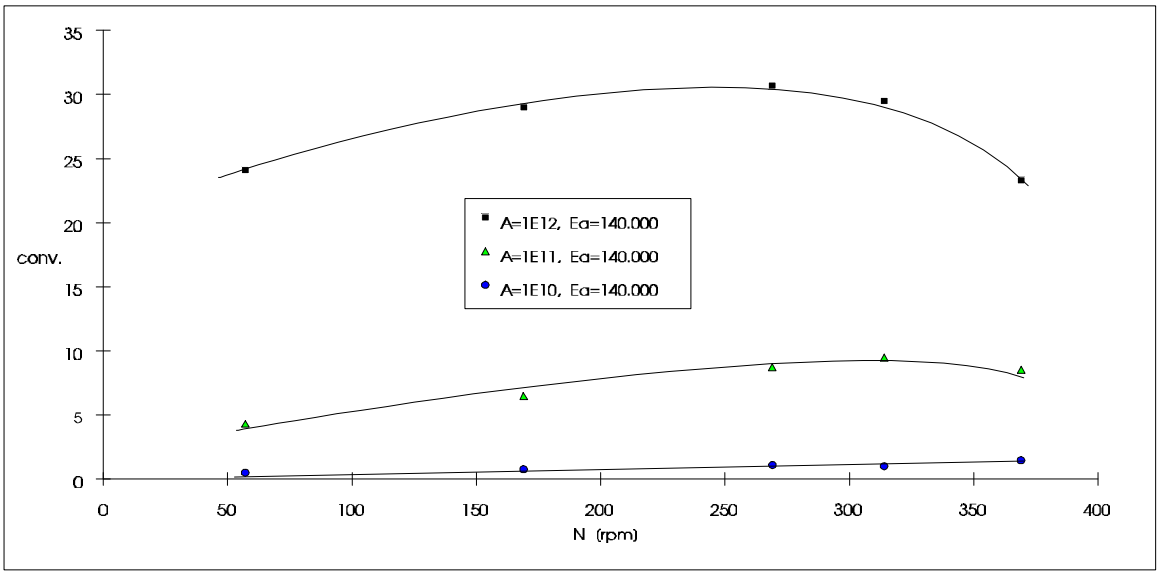

figure 1a The modelled conversion, T_b = 170 °C, M/I=100, [M] = 2100.5 [mole /m^3] number of kneading elements : 10, pressure buildup : 10 cm, Q = 1 kg/h.

Note that :

For a slow reaction the measured conversion is constant or decreases (figure 1a) and for a fast reaction the conversion increases with increasing rotation speeds (figure 1b). These phenomena are due to the fact that with increasing rotation speed the size of the dispersed phase decreases (chapter 7) and the temperature of the melt increases (chapter 6).

The conversion of the reaction is relatively large if the screw geometry has a long pressure build up section, figure 1b. The temperature and the reaction velocity in this pressure build up section increase with rotation speed. Therefore the conversion of the monomer in the minor phase increases with rotation speed. The modelled conversions in figure 1a have the same trend as the three lower lines (measured values) in figure 1c.

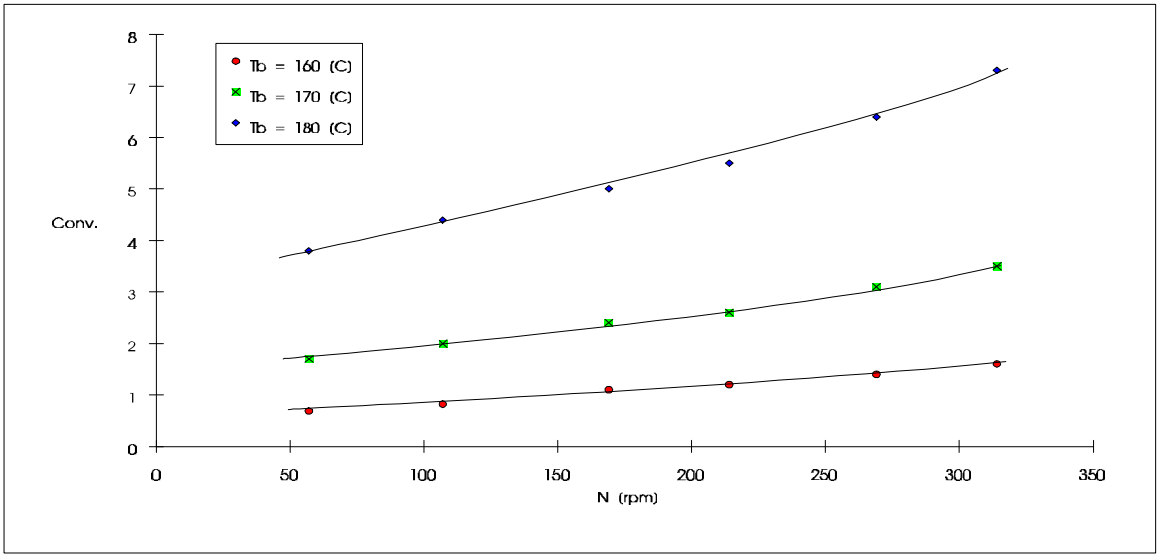

figure 1b *The modelled conversion in the dispersed phase, Q =1 kg/h, M/I =1000, number of kneading elements = 10, pressure build up section : 18 cm.*

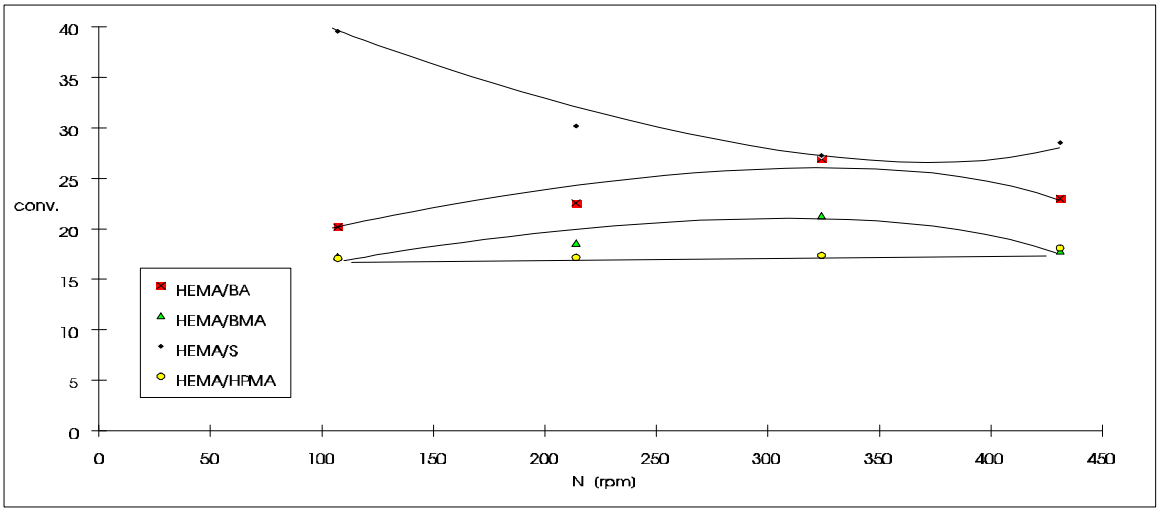

figure 1c *The measured conversion, M/I = 1000, T_b=150 °C, Q = 1 [kg/h], number of kneading element : 10, length of the pressure build up section = 32 cm.*

2 Experimental set up, *the extruder.*

Polystyrene and high density polyethylene or polypropylene are mixed in an intermeshing corotating twin screw extruder with a diameter of 50 mm and a length of 1200 mm (APV-Baker), figure 2. The extruder is operated at a rotation speed between 50 and 400 rpm and has a solids feed port in the first section. In most cases we focus on PS/HDPE (95 % / 5 %) blends.

2.1 Experimental set up, *the materials.*

The process studied is reactive compounding of high density polyethylene (HDPE, accurel, AKZO-NOBEL) or polypropylene (PP) with polystyrene (A in figure 2) (PS, ELF-ATOCHEM). Monomer and initiator (Trigonox 145) are dissolved in HDPE or PP (B in figure 2). In our first experiment Butylmethacrylate (BMA) has been chosen to be dissolved in HDPE (figure 3).

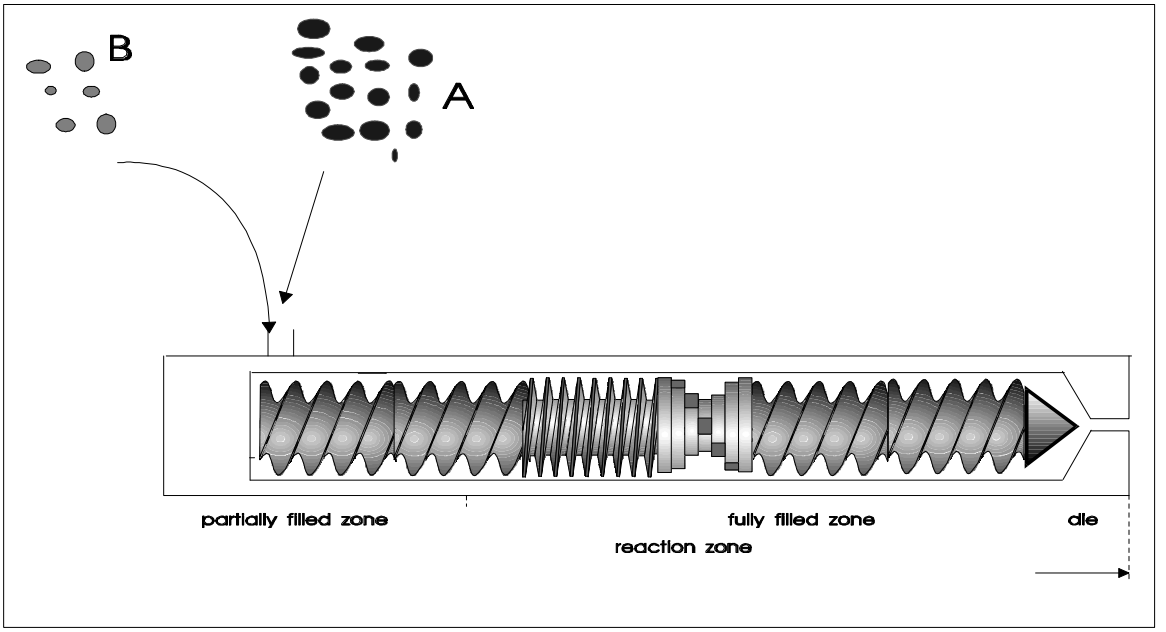

figure 2 Reactive compounding in the extruder

Additional experiments have been performed where the dissolved monomer consisted of hydroxy-propyl-methacrylate (HPMA), Butylacrylate (BA), Hydroxy-ethylene-methacrylate (HEMA), and Styrene (S), and mixtures of these monomers. Unless stated otherwise the barrel temperature of the extruder is 150 °C, the rotational speed is 57 rpm, M/I ratio is 1000, the concentration of monomer in the dispersed phase (HDPE or PP) [m] is 30 % by weight, and the throughput is 1 kg/h. The first transporting section is 40 cm, the pressure build up

section 32.5, the kneading section 12.5 cm, and the last transporting section 37.5 cm. Samples are cooled directly in liquid nitrogen when the blend leaves the extruder to prevent further changes (such as reaction of the monomer or changes of the morphology).
The initiator or the mixture of the initiator and the liquid monomer is dissolved into HDPE. This material was tumble mixed with PS (for example 10 mass % HDPE in 90 mass % PS by weight) and successively fed to the extruder.

2.2 Analysis.

In order to separate PS from HDPE we dissolve the samples, which are taken directly from the die of the extruder, in THF. We can separate the PS, which is solved in THF, from the HDPE, which is not solved. For the extraction we use a Soxtec system HT 2, 1045 Extraction Unit, Tecator Extraction thimbles (33*80 mm, Schleicher & Schuell). The grafting of monomer on HDPE is determined by measuring the amount of oxygen present in the separated dispersed phase of the blend. The tensile tests were done according to ASTM D1708 at a crosshead speed of 10 mm/min on a tensile tester Instron tensile tester at room temperature. Tensile specimens of the obtained blends were prepared by compression molding at 180 °C. Since the material made with our method might replace high impact polystyrene (HIPS) impact test are also of interest. Since impact properties are important in many applications of materials Notched-Izod (NI) values have been measured with a Zwick impact tester. Note that the values for impact strength must be multiplied by 1/0.03 due to sample dimensions. It appeared that the results from impact tests are very sensitive to small changes in the morphology of the material as well as small changes in the test piece. A NI measurement of 0.15 in the graphs in this thesis corresponds to a Notched Izod value of 5 which is comparable with the NI value of HIPS.

3 Results.

For improved toughness and impact strength of the blend the reaction is found to be of vital importance. In order to gain a better understanding the conversion of the monomer in the dispersed phase will be studied further. Rotational speed is one of the most important extruder parameters since it influences the conversion of monomer in the dispersed phase but also directly the size of the dispersed phase.
A blend of PS/HDPE with BMA monomer has been produced with the method described in chapter 1. From observations with SEM (figure 3) we find that the blend produced with reactive compatibilsation differs from the blend which has been described in chapter 7 because the size of the dispersed phase is smaller.

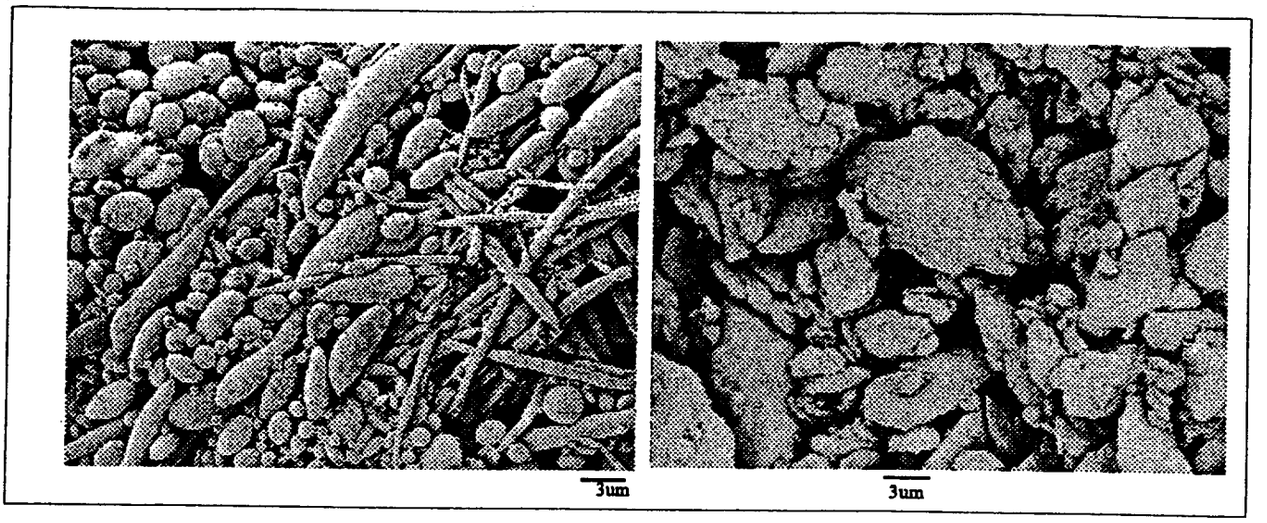

figure 3 PS/HDPE blend; BMA in HDPE; PS/PET blend, T_b = 200 °C, Q = 1.3 kg/h.

3.1 Material choice for the dispersed and matrix phase.

Monomer and initiator are added into the pores of accurel. Accurel is a porous type of granule of HDPE produced by AKZO-NOBEL. PS and Accurel are fed together into the extruder.

3.2 Material properties versus processing conditions.

The screw geometry has been shown in figure 12, chapter 8. A blend of PS/HDPE, produced with this screw geometry by mere physical compounding, is usually extremely brittle and has an elongation at break of a few percent. However tensile tests of the materials, made by reactive compounding, show a strong reproducible increase in elongation at break when the amount of HDPE increases from 1 to 5 percent, figure 4a. These values are very large if we compare them with the results of Kroeze (figure 1 chapter 3 of Ref. 6). The test speed in these tests was 10 mm/min.

In figure 4b the elongation at break has a maximum and decreases if the rotation speed is larger than 150 rpm. For the same samples the stress at maximum load increases while the toughness decreases. Compatibilsation of these samples decreases because their production temperature was to high. The optimal barrel temperature is 150 °C for this process when HPMA/BMA or BA/S is the monomer. Usually the maximum stress at load, of the samples made with the method described in this thesis, decreases slightly from 30 to 28 MPa if the elongation at break increases.

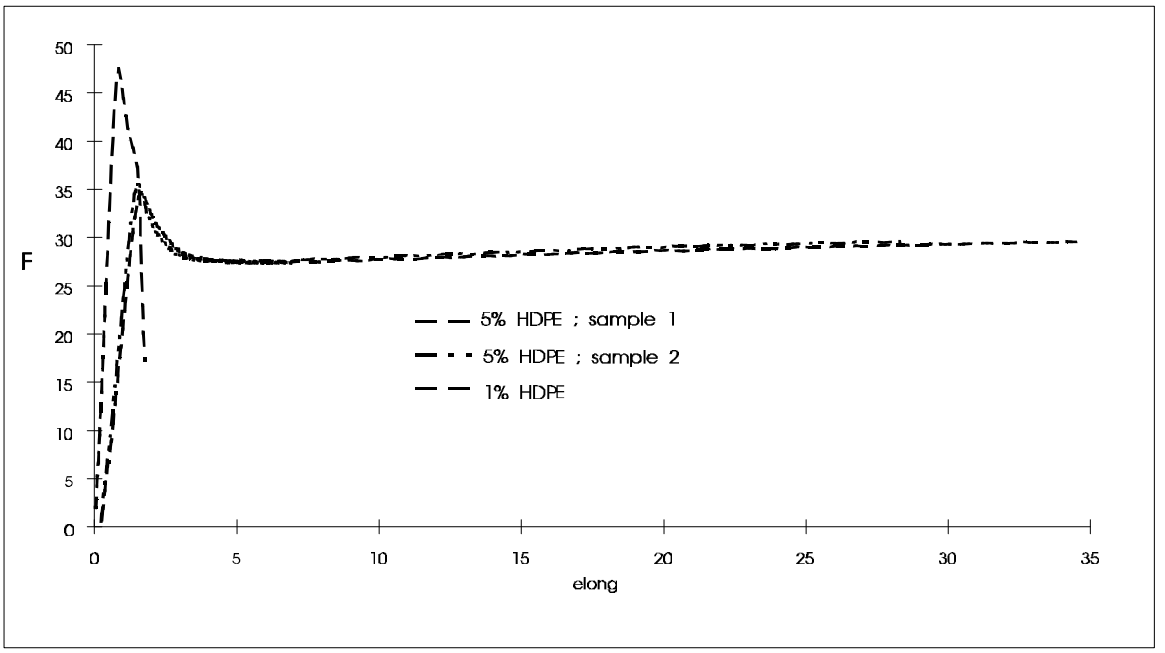

figure 4a Stress (F)-strain curve of a reactive blend with 1 and 5 % HDPE as the dispersed phase (in HDPE 10% monomer BMA has been absorbed), T_b= 180 ^oC, Q = 1.3 kg/h.

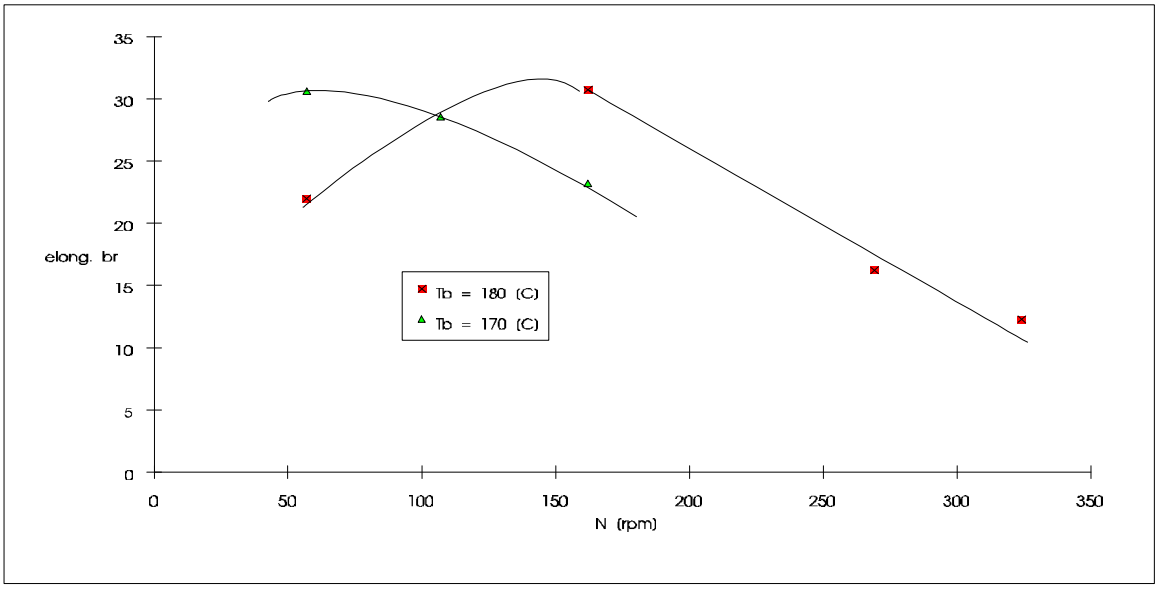

figure 4b Elongation at break - rotation speed , HDPE : 5%, HPMA/BMA (30 %) , Q= 1.3 kg/h .

In a few cases the maximum stress increases with the rotation speed of the screws (figure 4c). We found that this only is the case if the elongation at break decreases with increasing rotation speed. The influence of the percentage dispersed phase, the conversion of monomer in the

dispersed phase, the structure of the alloying agent formed and the size of the dispersed phase have been investigated.

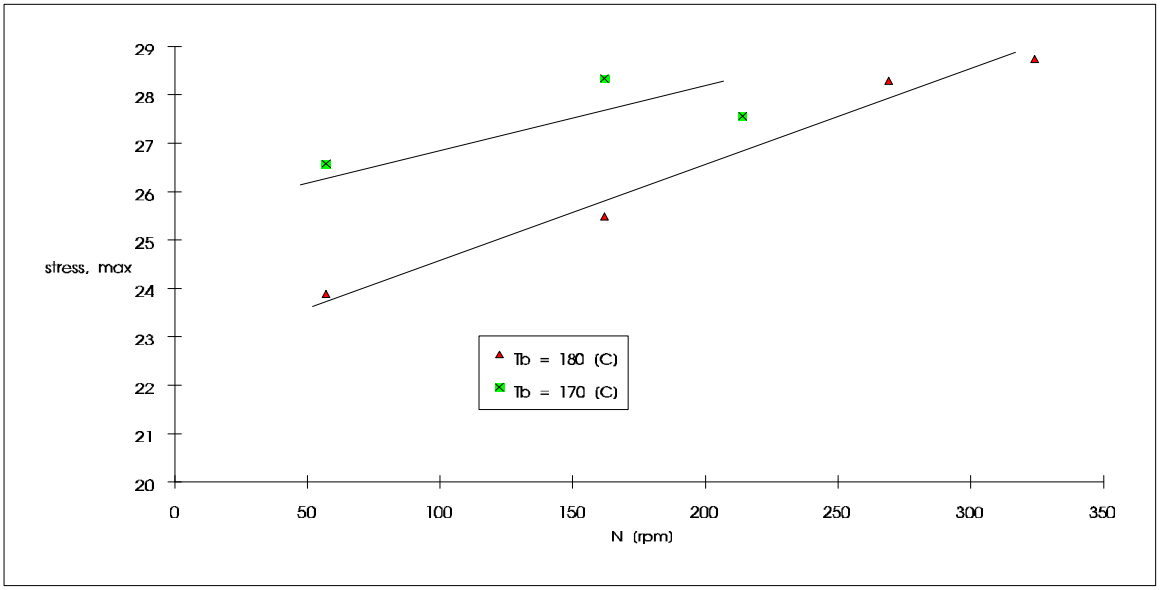

figure 4c Stress at maximum load - rotation speed [rpm]; HDPE : 10% BA/S 10%, M/I = 10000, Q = 1.3 kg/h.

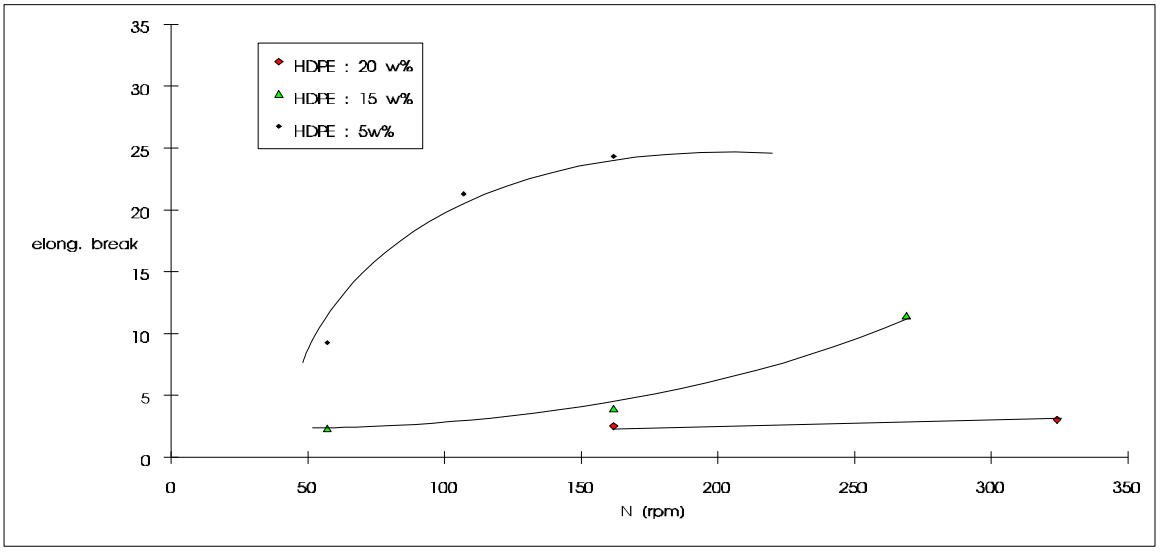

figure 4d *Elongation at break - rotation speed (N), M/I = 500, HPMA/BMA (30 %) , Q= 1.3 kg/h, blend PS/HDPE, T_b = 170 °C, Trigonox T .*

The blend with 1 percent HDPE in figure 4a has a much smaller elongation at break as the blend with 5 percent dispersed phase (figure 4a and figure 4d). The elongation at break decreases with increasing percentage dispersed phase if more than 5 % dispersed phase is mixed in. Coalescence increases if the dispersed phase is more than 5 % HDPE.

Toughness of a blend is found by calculating the area under the tensile curve (figure 4a). The toughness of reactive blends has a maximum as a function of the rotation speed as shown in figure 5. However the most important observation is that all materials have a strongly improved toughness compared with polystyrene (pure PS : T=0.4).

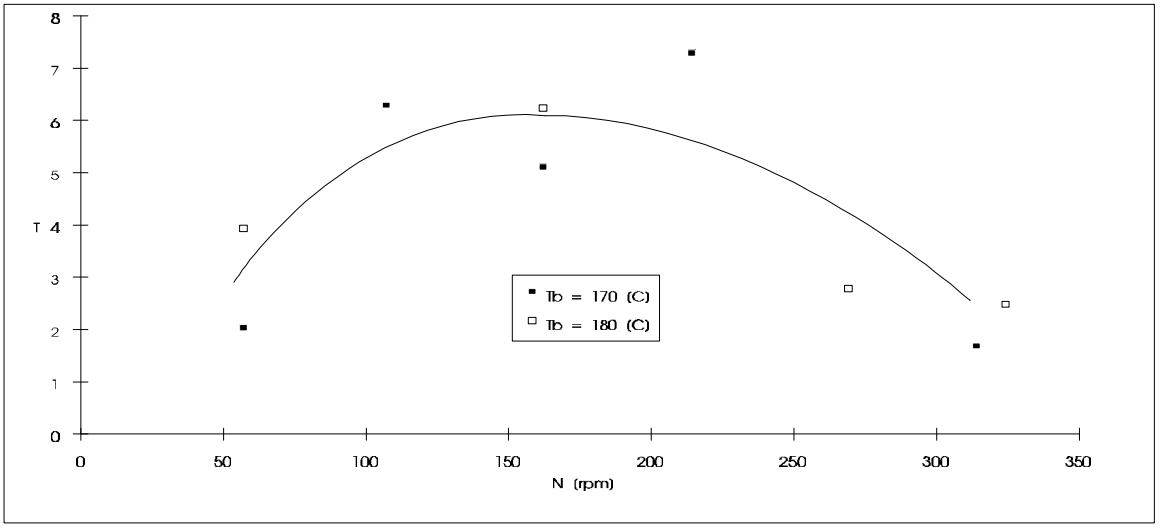

figure 5 Toughness - rotation speed [rpm] ; HPMA/BMA, 10% , M/I : 10000, Q = 1.3 kg/h, *T_b = 170 °C, HDPE = 15 %.*

3.3 Toughness and elongation at break.

In the literature it is usually found that for radical polymerisation the molecular weight increases when the monomer/initiator ratio increases. We expect the same to be valid for the formation of the graft copolymer (the compatibiliser to be formed) in the dispersed phase. To obtain an improvement of the toughness of the blend it is important that the alloying agent is formed in the polymer of the minor phase and more specific is present in the interfacial area. Its molecular weight must be larger than a critical value of the molecular weight between entanglements (M_e) as described by Creton, Kramer and Hadziioannou (5).

Larger Toughness at lower initiator concentration in figure 6a can only be explained by a more effective alloying agent. For this we assume that the reaction velocity decreases and the length of the graft copolymer increases (forming a more effective alloying agent) when the monomer/initiator concentration increases. Note that the samples with the lowest initiator concentration have the largest toughness (T). This is expected since the M_w of the alloying agent must exceed M_e as mentioned by Creton *et al* (5) and the M_w is larger when M/I is larger. In the previous chapters we have found that the conversion of the reaction decreases with increasing M/I but a higher concentration of alloying agent does not cause a larger

toughness. This is confirmed by the fact that also no influence of the conversion in the dispersed phase on the Notched Izod impact values is found in figure 10 (this chapter).

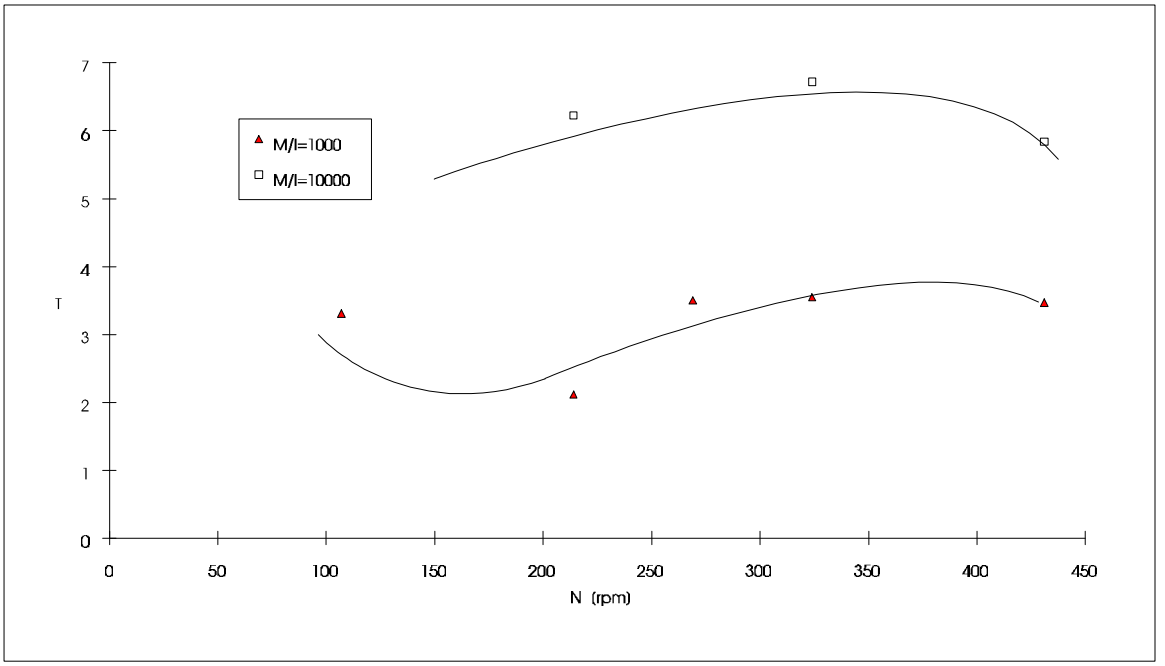

figure 6a *Toughness - rotation speed [rpm], T_b = 170 °C, HDPE = 15 %, HPMA/BMA.*

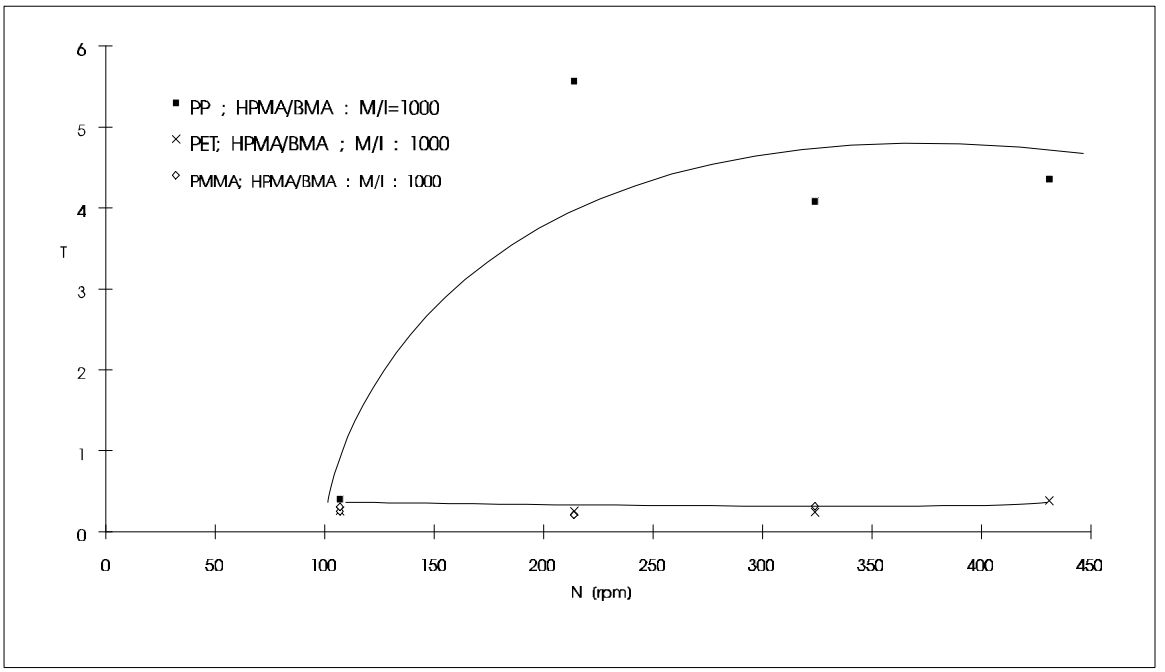

figure 6b *Toughness - rotation speed [rpm] for several material choices of the dispersed phase, PP, PET, PMMA.*

To determine whether the material choice of the dispersed phase is important PET and PMMA have been used for the dispersed phase in figure 6b (instead of HDPE or PP). In this case (PET, PMMA : T_g > 20 °C) no improvements in mechanical properties have been found.
From what we found so far we might conclude that the toughness and impact value of a blend probably is influenced by a combination of parameters such as the size of the dispersed phase, the molecular weight, and the concentration of the alloying agent in the polymer of the minor phase. No improvement is found when PET or PMMA is the dispersed phase which may be due to the fact that HDPE and PP are (partially crystalline) rubbers while PET and PMMA are not. Another possibility could have been that the dispersed phase was not small enough in the case of PET or PMMA. Therefore the size of the dispersed phase of the PS/PET and PS/PMMA blend has been measured with SEM (table 1, chapter 10) but was found to be comparable with the size for PS/HDPE and PS/PP blends. Possibly another condition for improved mechanical properties of the blend is that the dispersed phase must have a T_g smaller than 20 °C. Moreover the chemical bonding between the minor phase and the major phase must be sufficiently strong.

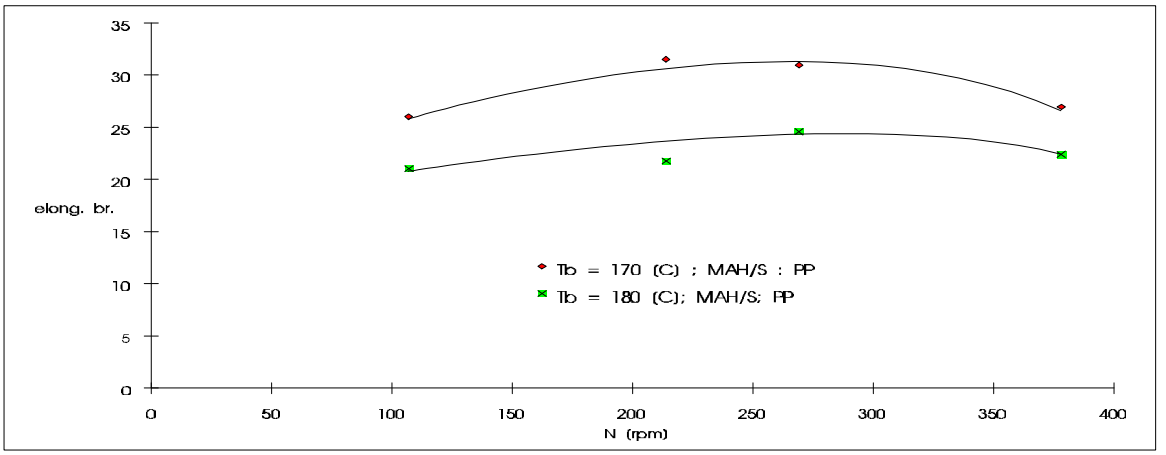

figure 7 *Elongation at break - rotation speed [rpm], blend PS/PP,* MAH/S (ratio 1:1)

The elongation at break, Notched Izod impact strength and toughness of the blend were almost constant as a function of the rotation speed of the extruder, figure 7 and 8a. Probably the graft-copolymerisation has a sufficiently high conversion and the alloying agent formed in these experiments is effective enough.

3.4 The influence of rotation speed on the Notched-Izod impact values.

In figure 8a both toughness and impact value increase. The large improvement is remarkable since only a small monomer concentration and a small amount of HDPE is used. Probably

there is a relation between the length of the alloying agent in the dispersed phase and the mechanical properties such as toughness and impact value.

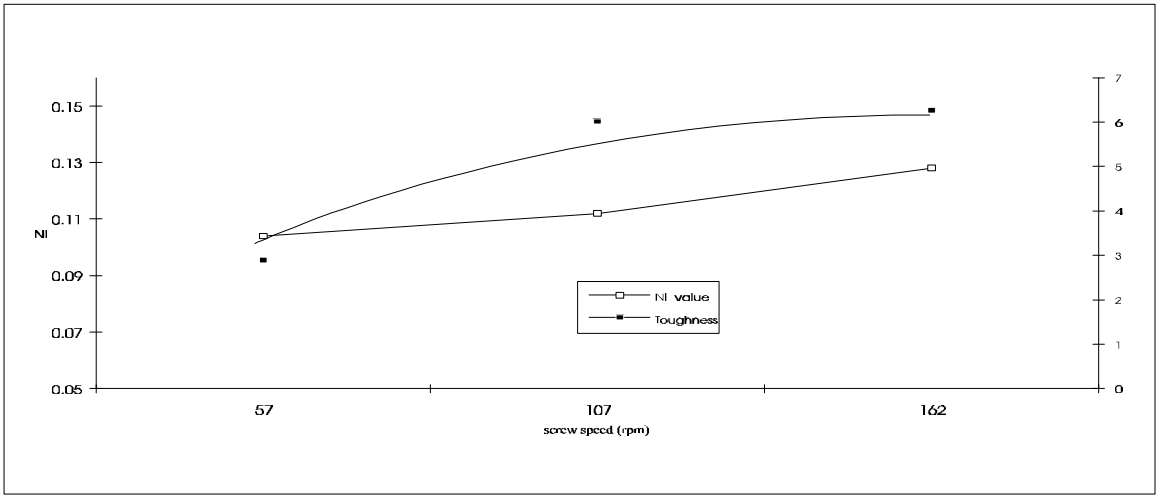

figure 8a *(NI) Impact and toughness - rotation speed [rpm] , 5% HPMA/BMA, T_b = 170 °C, PS (95%)/HDPE (5%), [m]=5%.*

It is of great practical use if a product made out of a plastic does not break when it falls. The chance for a product to break is determined by its response to a fast impact force and therefore the (Notched) Impact value is at least as important as the elongation at break.

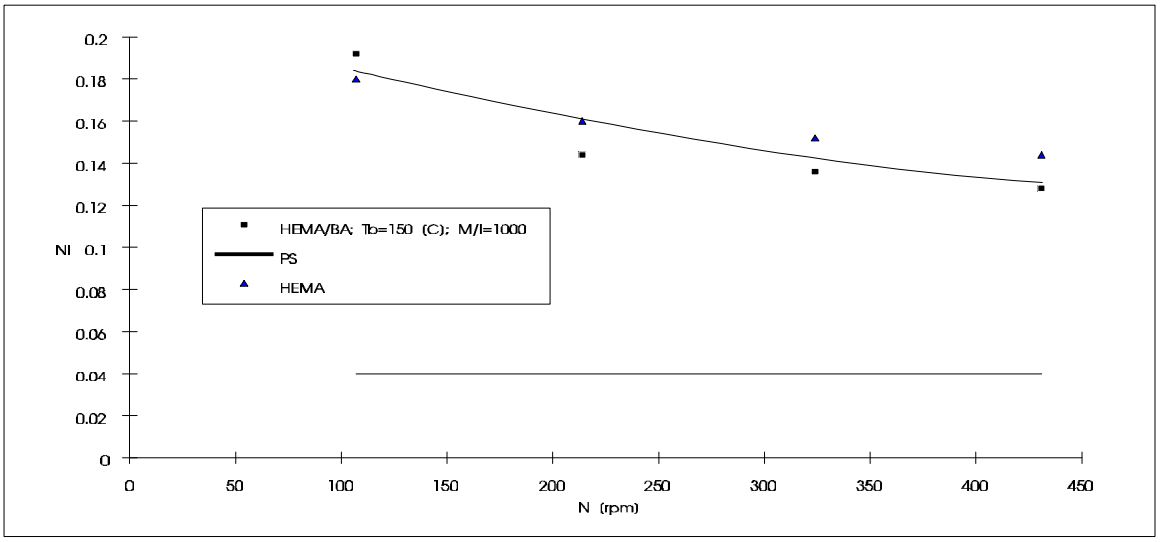

figure 8b *Notched Izod values, T_b = 150 ° C, Q : 1.3 kg/h, HEMA/BA and HEMA, M/I = 1000, PS/HDPE (90 % / 5 %), [m]= 30 %.*

The Notched Izod value of the reactive blend is at least three times as large as the Notched Izod value of PS, figure 8a and 8b. For most combinations of reactive mixtures it is almost

constant as a function of rotation speed of the screw (figure 9). It is also remarkable that the Notched Izod values for reactive blends made with different monomers have only slightly different values. The NI value of pure PS is between 0.03 and 0.04 depending on the barrel temperature.

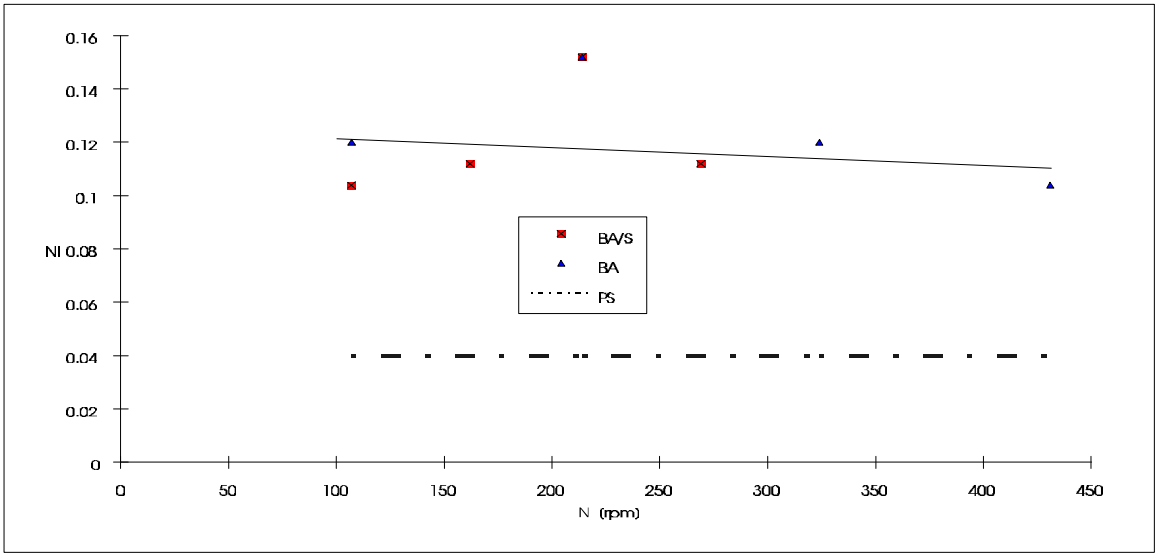

figure 9 ; Notched Izod - rotation speed [rpm] , pure PS and reactive blends , monomers : BA/S and S , (M/I = 1000).

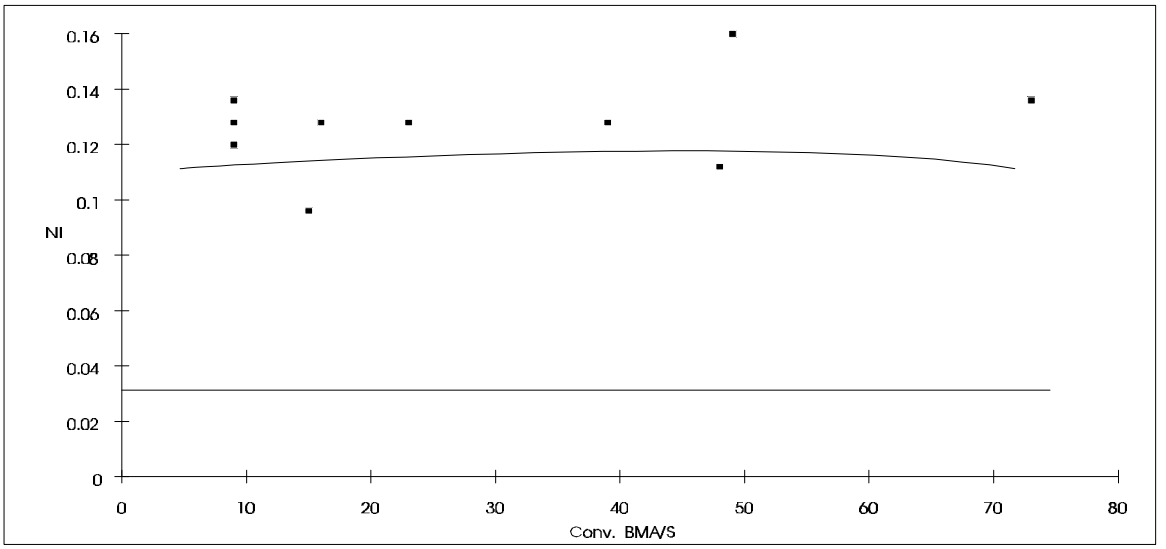

figure 10 Notched Izod Impact value versus the conversion of BMA/S in the dispersed phase.

The impact strength is almost constant as a function of the conversion of the monomer in the dispersed phase, figure 10. Since this has no influence on the impact values it is possible that the interface is already saturated with compatibiliser. With increasing rotation speed the

notched Izod impact value decreases and the conversion increases as shown in figure 11. Again the interface is already saturated with compatibiliser and a further increase of the conversion means a less efficient alloying agent.

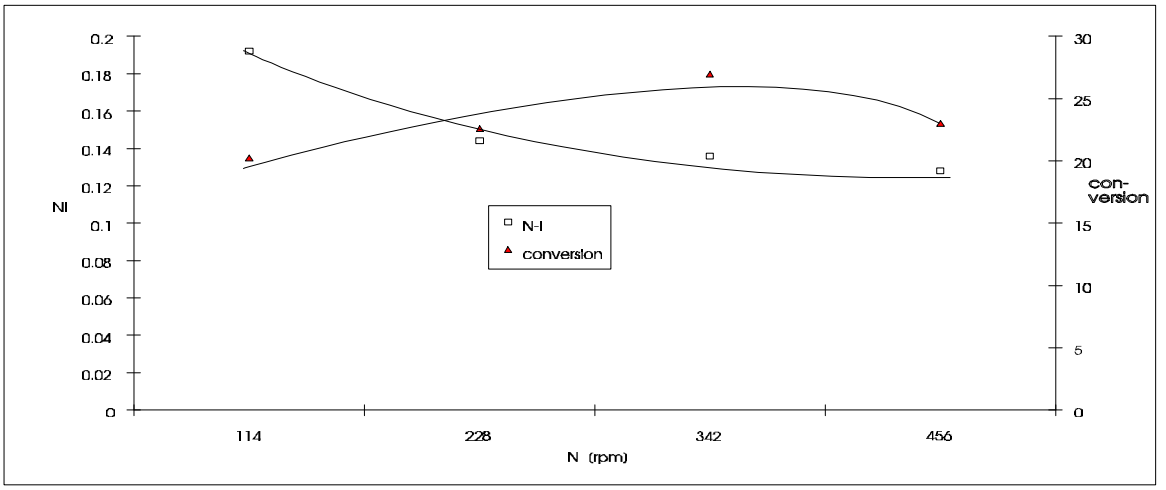

figure 11 Impact strength and conversion - rotation speed [rpm], HEMA/BMA.

Again the most plausible explanation for the relative large NI value relative to PS is that a chemical link between the matrix phase (PS) and the dispersed phase (HDPE) is formed. However note that some unreacted monomer is still present if the conversion is low, figure 11.

3.5 Impact values versus conversion and rotation speed.

From figure 12a we might conclude that the Notched Izod impact value of our blend increases because the conversion increases and a graft copolymer is formed in the dispersed phase. Unfortunately it is not this simple since the Notched Izod impact strength does not always increase with increasing conversion of HPMA/BMA in the dispersed phase of the blend, figure 12b. In the samples made with small rotation speed the conversion usually was small and mixing poor which in many cases means poor compatibilsation. This might explain the small NI values at small conversions in figure 12a. This also is due to a large concentration of unreacted monomer which is still present in the dispersed phase.

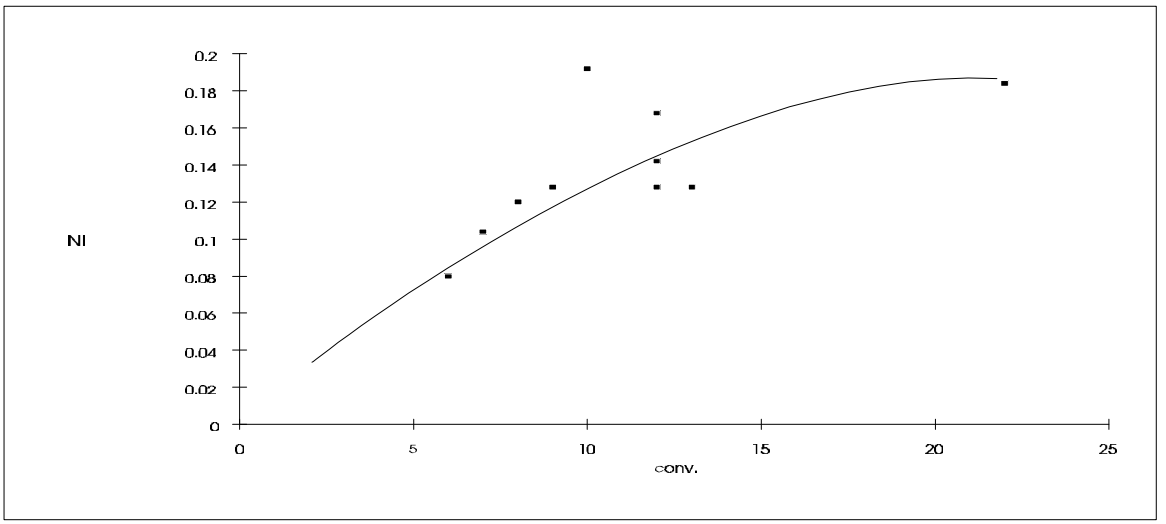

figure 12a *The Notched-Izod impact strength versus the conversion of HPMA/BMA, PS (95%)/HDPE (5%), [m]=30%.*

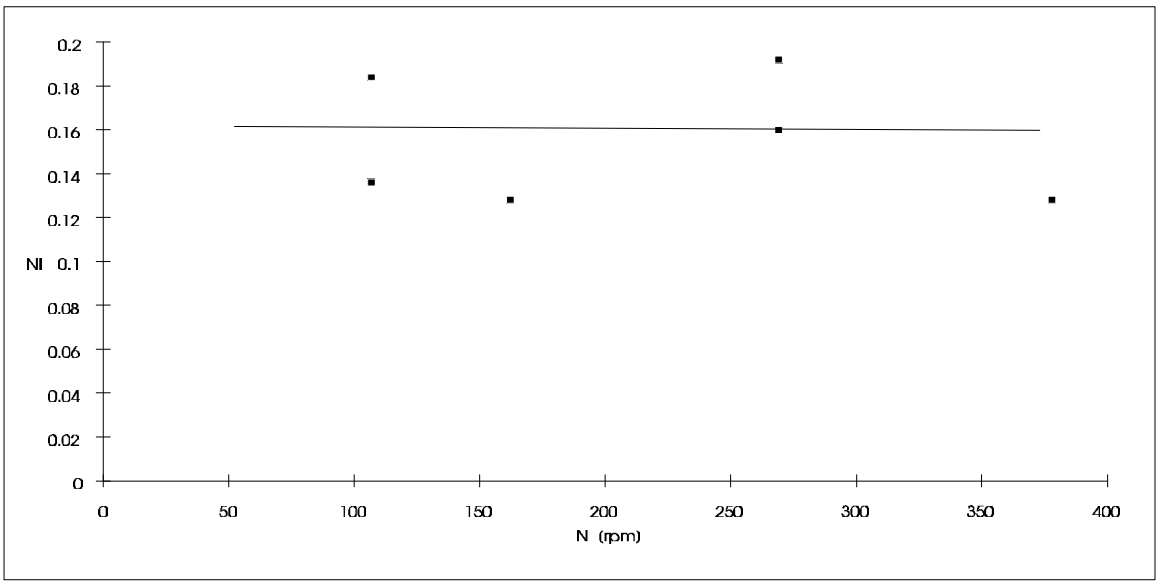

figure 12b *The Notched-Izod impact strength versus the rotation speed, HPMA/BMA, PS (95%)/HDPE (5%), [m]=10%.*

In contrast with figure 12a the Notched Izod impact strength in most cases is constant with increasing rotation speed (figure 12b).

3.6 The relation between elongation at break, conversion, and an efficient alloying agent.

Both an increase and a small decrease of the elongation at break can be seen in figure 13.

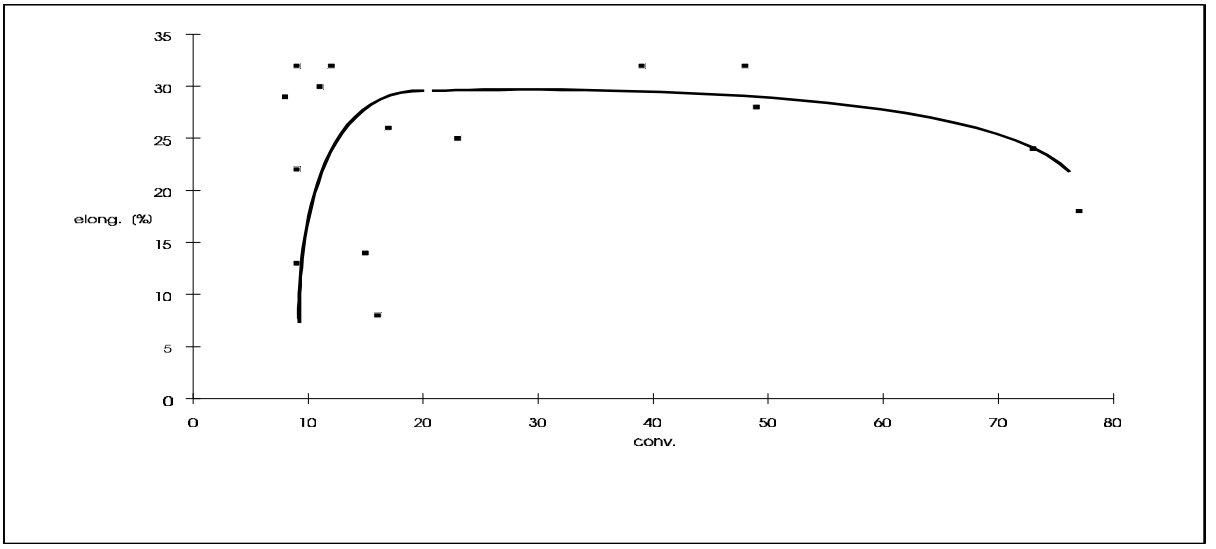

figure 13 The elongation at break - the conversion of BMA/S PS (95%)/HDPE (5%).

When BMA/S is absorbed in the dispersed phase the elongation at break is almost constant at conversions larger than 10 % and smaller than 50 %, figure 13. If the conversion is larger than 50 % more graft-copolymer has been formed. Clearly a less effective alloying agent has been formed causing a decreased toughness of the blend at a conversion exceeding 50 %.
The influence of the processing conditions and the choice of monomer on the elongation at break will be described below. Usually it is found that the elongation at break increases with increasing rotation speed (figure 14a, 14b, and figure 14 c).

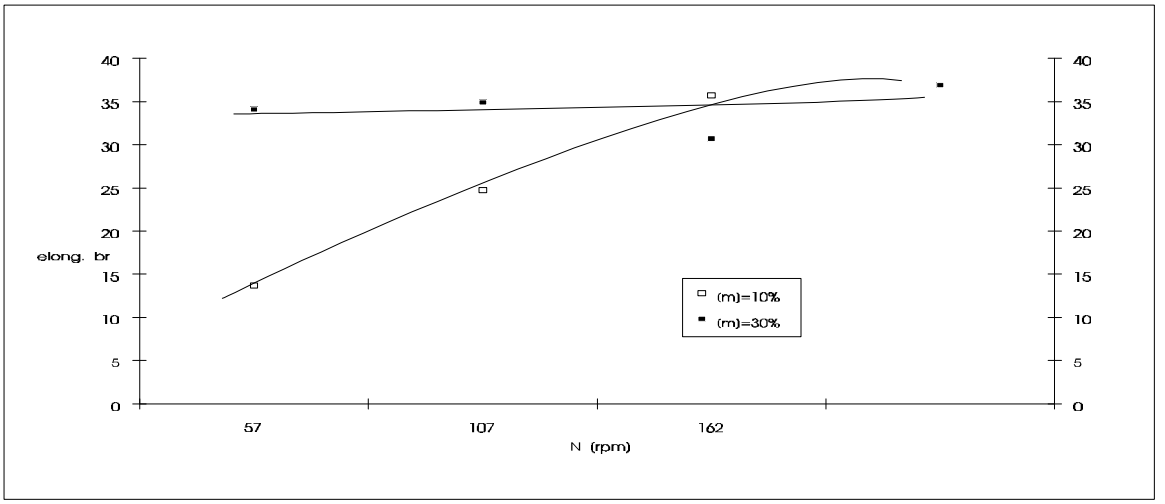

figure 14a The elongation at break - rotation speed [rpm] , monomer : HPMA/BMA, M/I=1000, Q = 0.5 kg/h, T_b = 170 ºC, 10 and 30 % monomer absorbed in the dispersed phase, PS (95%)/HDPE (5%).

In figure 14a the elongation at break increases with increasing rotation speed if 10 % HPMA/BMA is absorbed in the dispersed phase while the M/I is relatively small (1000). At this initiator concentration the elongation at break is large for all rotation speeds if 30 % HPMA/BMA is absorbed in the dispersed phase.

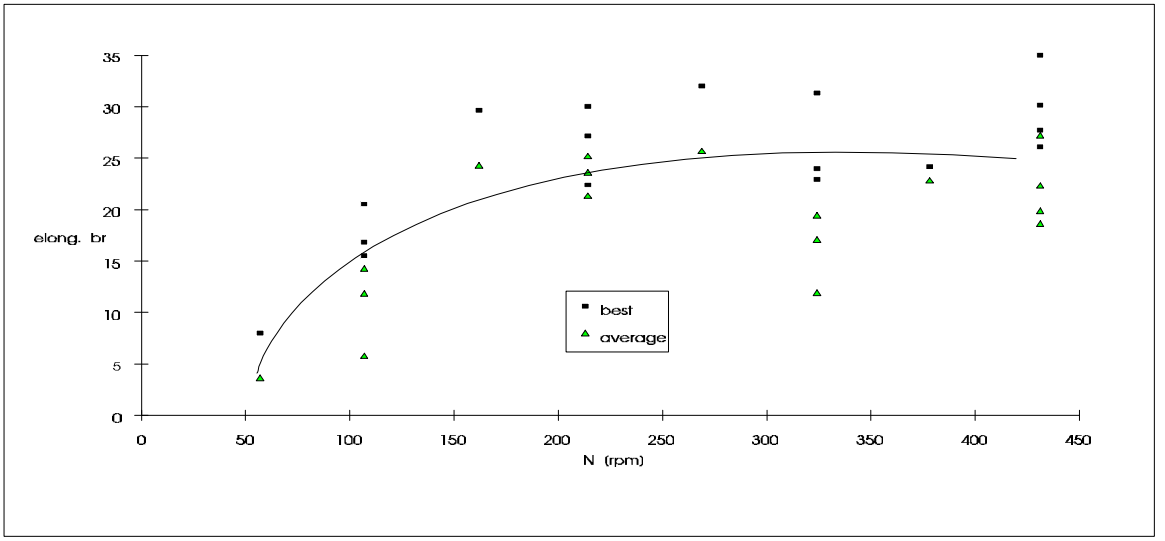

figure 14b The elongation at break - rotation speed [rpm], monomer : HPMA/BMA, M/I=10000, T_b = 160 ºC, 30 % monomer absorbed in the dispersed phase, PS (95%)/HDPE (5%).

In figure 14b the elongation at break increases with increasing rotation speed and reaches a value of 30 %. In this case the barrel temperature (T_b) is 160 °C which is lower than the barrel temperature used to make the blends shown in figure 14a. Because the barrel temperature is lower in figure 14b the temperature in the melt which is measured in the pressure build up section is determined by viscous dissipation. It increases with increasing rotation speed. The reaction and increase of M_w of the alloying agent formed by the reaction takes place in the pressure build up section. The compatibilsation due to the alloying agent and therefore also the mixing increases when the barrel temperature is set to higher values. Since the efficiency of the alloying agent formed increases the elongation at break also increases.
In figure 14c the barrel temperature is again 160 °C and the initiator concentration has been varied. The temperatures in the pressure build up section were measured and were found to increase with increasing rotation speed. This is important since in this case the temperature of the melt determines the concentration and M_w of the graft copolymer formed.
Because the temperature in the melt determines the structure of the alloying agent the initiator concentration has no effect on the elongation at break in figure 14c.

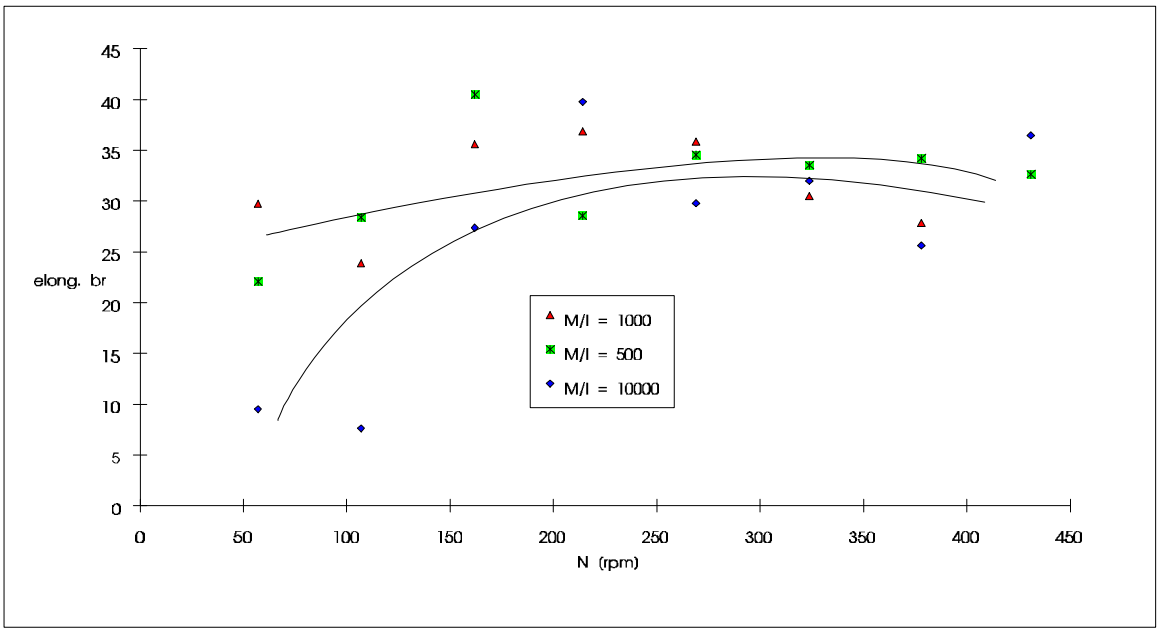

figure 14c The elongation at break - rotation speed [rpm], HPMA/BMA, T_b = 160 ˚C 30 % monomer absorbed in the dispersed phase, influence of the M/I ratio, PS (95%)/HDPE (5%).

Normally the M/I ratio must be large and is a very important parameter because it determines whether the alloying agent is effective, figure 14d. This is in contrast with figure 14c where the effect of the initiator concentration is not very clear.

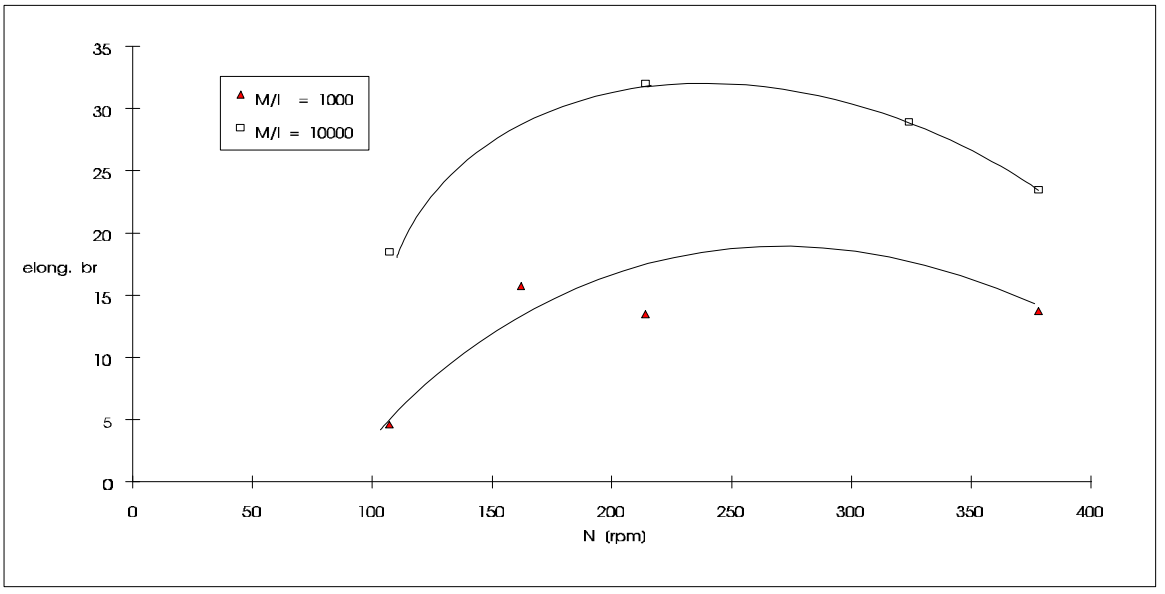

figure 14d The elongation at break - rotation speed [rpm], BMA/S, M/I=1000 and M/I= 10000, T_b = 160 °C, 30 % monomer absorbed in the dispersed phase , PS (90%)/HDPE (10%).

The choice of monomer is also important for the efficiency of the alloying agent since normally it is expected that HPMA/BMA-g-HDPE is a less efficient alloying agent than BMA/S-g-HPMA. Note that the styrene part of the copolymer can penetrate PS forming a bonding between matrix and dispersed phase. The influence of the M_w of the alloying agent is that a large difference in the elongation at break for different M/I ratio's is found in figure 14d.

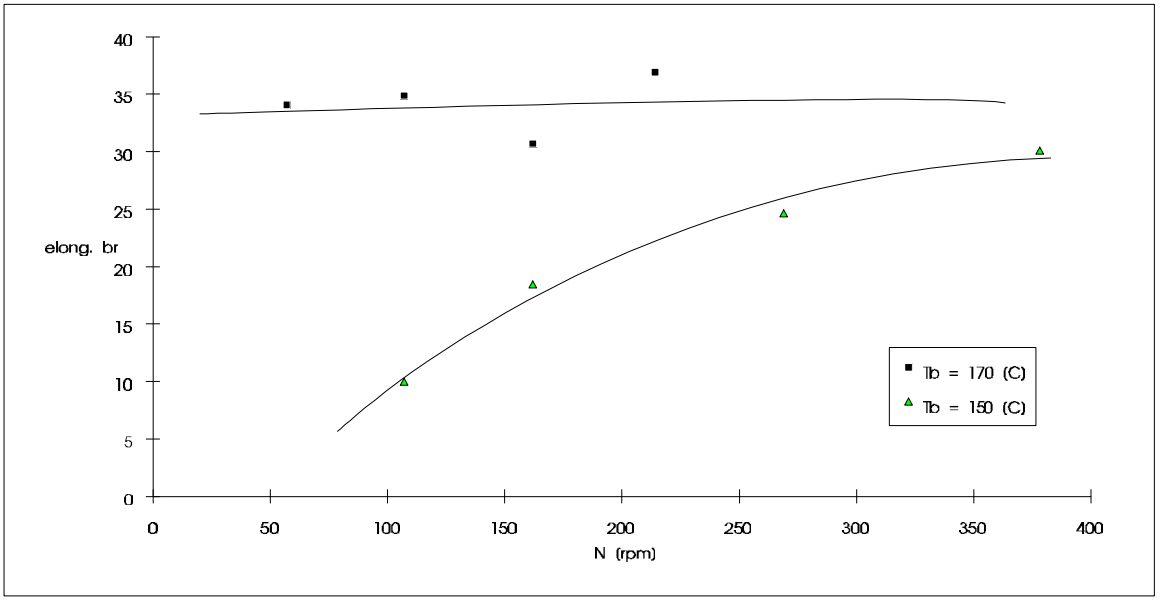

figure 14e The elongation at break - rotation speed [rpm], HPMA/BMA, M/I=1000, T_b = 150 °C and 170 °C, [m]=30 % monomer absorbed in the dispersed phase.

In figure 14e the blend (with HPMA/BMA as monomer) has a large elongation at break for all rotation speeds when the barrel temperature is 170 °C. This is not the case when the barrel temperature is 150 °C and the rotation speeds are small. This can be explained by the faster decomposition of the initiator at higher temperatures. Due to this the initiator concentration decreases faster at higher melt temperatures. A small initiator concentration means a larger M_w of the graft copolymer and a more efficient alloying agent.

4 Discussion.

It can be concluded that our method is fairly successful in improving the mechanical properties of the blend PS/HDPE and PS/PP. However more work is needed to better understand the relation between material properties, blend morphology, and reactive compounding.
Many more measurements were done for which also the concentration of monomer absorbed has been varied between 0.1 % and 30 % with respect to the mass % HDPE. On the average the influence of the monomer concentration was found to be relatively small. In all cases the mechanical properties were improved sufficiently. Because of this it seems profitable to use a

minimum amount of monomer in the dispersed phase which is easier for processing (feeding a wet sticky mixture of polymer and monomer into the extruder with the hopper is difficult). It is also better if we want to keep the amount of monomer remaining in the blend after reactive compounding to a minimum. So far we found that reactive compounding should be designed such that first the grafting of monomer in the dispersed phase occurs. This is done to make sure that most monomers react in the polymer of the minor phase. Therefore the screw geometry is designed such that the polymer mixture has a long residence time and a high temperature in the pressure build up section before entering the kneading section. Because of this, a large part of the monomer can react to form grafted-copolymer on the polymer chains of the dispersed phase. After passing through the pressure build-up section the blend passes through a kneading section decreasing the size of the dispersed phase. If the conversion of monomer in the dispersed phase is large enough the toughness of a PS/HDPE blend can be improved with reactive compounding. The influence of processing conditions and monomer/initiator ratio provides opportunities for optimisation.

Van der Sanden (3) has claimed that the distance between dispersed particles must be below 1 μm which was found to be difficult when more than 15 mass % HDPE was the dispersed phase due to coalescence during mixing. From SEM. it was found that in our blends the distance between the several spheres of the dispersed phase was much larger than the critical interparticle diameter. Possibly the properties of our blends can be further improved by forming a blend with a smaller interparticle distance between the several spheres of the dispersed phase and good adhesion between the matrix and the dispersed phase.

As a conclusion for most cases favourable conditions for tough mechanical properties are sufficient mixing, a higher temperature, larger M/I ratio, and a smaller monomer concentration. Because of the large amount of parameters which have an influence on the mechanical properties of the blend (conversion, molecular weight, size of the dispersed phase, choice of monomer) a general explanation of trends is not available yet.

The following theory can be considered for blends in which the major phase is amorphous :

The unreacted monomer in the neighbourhood of the dispersed phase also may have a toughening influence. The improvement of our new method of reactive compounding is not as large for NI measurements because the soft part of the blend (which is a monomer/polymer mixture) is to weak when the tests take place at much larger velocities. When under load, the PS part of a blend can deform but the stress must also be passed on to the dispersed (HDPE, or PP) phase by the adhesion between the matrix and the dispersed phase. Brittle breakage occurs if the stress can not be passed on at some interface (because of poor adhesion or a hard particle).

5 Conclusions.

The blends of PS/HDPE and PS/PP have strongly improved mechanical properties for all samples. The elongation at break of PS/HDPE blends made by reactive compounding is always very large. Also the Notched-Izod value of PS/HDPE blends is large (4 times as large as pure PS) because the reaction of monomer with the polymer of the minor phase improves the chemical bonding between the dispersed phase and the matrix phase while the size of the dispersed phase decreases. Unfortunately no direct evidence of the chemical bond between the dispersed and matrix phase was found.

The toughness of PS/HDPE and PS/PP blends is much larger than the toughness of PS. The stress at maximum load is about 30 MPa which is smaller than the value of pure PS. The morphology of the blend and the molecular weight and concentration of the alloying agent are likely candidates to directly influence the mechanical properties of the blend.

The molecular weight distribution of the graft copolymer formed is very important but not known in sufficient detail. The thermodynamics of monomers and graft copolymers captured in the dispersed phase is also not known. More experimental results are needed.

For application of these blends their material properties must be well defined and variances in impact values are usually not allowed. Therefore controlling the processing parameters and the conversion of the monomer in the dispersed phase is essential for the improvement of the toughness of the blend. The influence of extrusion parameters on the properties of the blend can be understood from the concentration and structure of the alloying agent in the polymer of the minor phase. The reactions of monomer and initiator of the minor phase will mostly influence this. The concentration of alloying agent in the polymer of the minor phase will decrease when less monomer is present in the polymer of the minor phase.

For practically all combinations of polymers it has great advantages to determine if the method described in this thesis can be applied. This is more cost effective than most conventional methods because it uses only the cheapest material such as monomers and initiators and in small amounts. The method is flexible and can therefore also be used for the recycling of many different polymers. However more research is needed. Part of this research should focus on methods to keep the amount of unreacted monomer (which is already small) below the ppm level.

Nomenclature

[m]	Monomer concentration in the dispersed phase	[mole /m^3 /s]
Conv.	Conversion of the reaction in the dispersed phase (grafted monomer)	%
M_w	Average molecular weight	[g/mole]
M_{wcr}	Critical average molecular weight	[g/mole]
M_e	Average molecular weight between entanglements	[g/mole]
M/I	Monomer over initiator ratio	[-]
N	Screw speed	[rpm]
NI	Notched Izod impact value (relative value)	[-]
Stress	Maximum stress at Yield	[MPa]
T	Toughness (surface under the tensile test curve)	[MPa]]
T_b	Temperature of the barrel	[°C]
Q	Throughput	[kg/h]
elong, break.	Elongation at break during a tensile test (velocity 10 mm/min)	[%]
Q	Throughput	[$m^3.s^{-1}$]

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